Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Kauzmann paradox and the crystallization of glass-forming melts

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ARTICLE INFO

Keywords:
Glass
Crystal nucleation
Kauzmann paradox

ABSTRACT

General relations for the dependence of the thermodynamic driving force of crystallization and the specific interfacial energy melt-crystal of critical crystal clusters on temperature and pressure are derived. Its application to the analysis of experimental data on crystal nucleation seems to support at a first glance a proposal by Kauzmann on the existence of a pseudo-spinodal curve in melt-crystallization. Provided this assumption is true, Kauzmann temperature (and for pressure-induced nucleation, the Kauzmann pressure) cannot be reached by a metastable liquid due to intensive crystallization processes occurring in its vicinity. However, such suggestion cannot be retained taking into account the kinetic terms (diffusion coefficients, viscosity) in the expression for the nucleation rate. The absence of a pseudo-spinodal in melt-crystallization can be verified also in an alternative way by considering the characteristic time scales of crystallization and relaxation. Finally, it is shown that the phenomenon denoted commonly as Kauzmann paradox is merely an untypical as compared to normal conditions type of behavior. Neither in its original formulation nor in its consequences it results in any contradictions with basic laws of nature. They are prevented either by normal (not associated with a pseudo-spinodal) crystallization or a conventional glass transition.

1. Introduction

The formation of crystallites in liquids caused by deviations of temperature or pressure from the respective liquid-crystal equilibrium states is a realization of first-order phase transformations, which is of particular importance in a variety of processes in nature and technological applications. In order to describe appropriately such processes, the thermodynamic driving force and the specific interfacial energy for the respective phase transition have to be known being two of the main ingredients of the theoretical description [1–4]. The first of these problems - the determination of the thermodynamic driving force - has been intensively discussed for crystallization caused by variations of temperature. It is much less analyzed for crystallization caused by variations of pressure [5] or simultaneously of both pressure and temperature [6]. The second of the mentioned problems - the specification of the specific interfacial energy melt-crystal - is a more complex task as compared to the first one since even for planar interfaces the experimental determination of this quantity is not possible with an accuracy required for the description of nucleation and appropriate theoretical approaches have to be advanced in order to fill this gap [7–9].

By the mentioned reasons, as a first topic of the present paper, results of the recent work devoted to these problems [10–13] are briefly reviewed and advanced, i.e., expressions for the thermodynamic driving force and the specific interfacial energy in dependence on both pressure and temperature are formulated. As one of the applications of these expressions the question has been analyzed in [14–16], whether certain peculiarities in the dependence of the work of critical cluster formation on temperature observed widely experimentally can be explained by classical nucleation theory (CNT) employing these results or whether other features of crystal nucleation at large undercooling have to be accounted for not incorporated commonly into CNT (see also [17–20]). Here we will employ these results for an analysis of the interplay of crystal nucleation and glass transition processes, of Kauzmann's suggestion of the existence of a pseudo-spinodal at low temperatures characterized by intensive crystal nucleation, and of possible ways of resolution of the Kauzmann paradox. All three topics represent important problems in the theoretical description of the vitreous state and of melt crystallization widely discussed in the literature.

Indeed, a variety of specific features of crystal nucleation and growth as compared with other types of first-order phase

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https://doi.org/10.1016/j.jnoncrysol.2017.11.045
Received 31 August 2017; Received in revised form 10 October 2017; Accepted 26 November 2017
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Please cite this article as: Schmelzer, J.W.P., Journal of Non-Crystalline Solids (2017), https://doi.org/10.1016/j.jnoncrysol.2017.11.045